

EFFECTS OF GRAIN SIZE REDUCTION ON THE ELECTROANALYTICAL PERFORMANCE OF CONDUCTIVE DIAMOND ELECTRODE DEPOSITED IN CH₄/H₂ GAS MIXTURE

K. L. Soh, W. P. Kang, J. L. Davidson, Y. M. Wong, B. K. Choi

Department of Electrical and Computer Engineering, Vanderbilt University, Nashville, TN 37235, USA.

D. E. Cliffler

Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA.

Keywords: Conductive diamond electrode, electroanalytical performance, nanocrystalline diamond, grain boundary, ferrocyanide.

Abstract

Diamond is one of the most recent carbon allotropes to find utility in electrochemical analysis. Boron-doped polycrystalline diamond planar electrodes synthesized by chemical vapor deposition (CVD) methods exhibit many properties of an excellent electrode such as low non-Faradaic current over a wide working potential window, quasireversible to reversible kinetics and large signal-to-background ratio for several redox system without need for surface pretreatment, excellent morphological and structural stability at extreme potentials and current densities, and long-term stability [1]. In addition, its resistance to surface fouling and chemical inertness also make it well suited for application in harsh environments and *in vivo* conditions.

The electrochemical behavior of the diamond electrode is governed by its physicochemical properties, which in turn is largely influenced by the CVD deposition process. Variation of deposition parameters and types of plasma used can be manipulated to affect the morphology of the diamond crystallites and thus cause a modification of the surface chemistry which will determine the course of application. This work reports on the effects of grain size reduction on the electroanalytical performance of conductive diamond electrode deposited in CH₄/H₂ gas mixture. Grain size reduction was achieved by decreasing the CH₄ flow rate while keeping other fabrication parameters constant. The diamond deposition was performed at microwave power 5 kW, temperature 800° C, pressure 120 torr, H₂ flow rate 478 sccm, and varying CH₄ flow rate 15, 10, 5 and 1 sccm. Boron doping was achieved using a p-type gaseous dopant; trimethylboron (TMB) = 20 sccm. Diamond deposition duration was two hours.

Figure 1 (a) shows the SEM micrographs of diamond electrodes deposited using 15, 10, 5 and 1 sccm CH₄. Diamond crystallites transitioned from microcrystalline to nanocrystalline when CH₄ flow rates were decreased. Nanocrystallinity of diamond electrode was achieved at CH₄ = 1 sccm as supported by Raman spectroscopy. Figure 1 (b) shows the Raman spectra of the four diamond electrodes. As CH₄ flow rate was decreased, the diamond peak at 1332 cm⁻¹ broadened due to reduction in grain size and increase in defects [2]. The peak intensity at ~1615 cm⁻¹ results from graphitic sp² bonds at the grain boundary [2]. As microcrystalline diamond (MCD) transitioned into nanocrystalline diamond (NCD), the fraction of grain boundary increased thus causing the ratio of I₁₃₃₂/I₁₆₁₅ to fall. At CH₄ = 1 sccm, the diamond peak was less resolved. Additional peaks were also observed and two of importance are the shoulders at ~1160 cm⁻¹ and ~1450 cm⁻¹ which were characteristic of NCD [3].

Figure 2 (a)(i) shows the cyclic voltammograms for the redox reaction of 1 mM Fe(CN)₆⁴⁻ in 0.1 M KNO₃ at a scan rate of 10 mV/s for the four electrodes. A plot of oxidation peak current, *i*_{p,ox} vs. square root of scan rate, *v*^{1/2} is linear (not shown), indicative of linear diffusion-controlled process. Table 1 shows that the diamond electrodes displayed higher resistance (*R*), lower oxidation peak current (*i*_{p,ox}) and larger peak separation (ΔE_p) for oxidation of ferrocyanide, Fe(CN)₆⁴⁻ with decreasing grain size. The electroanalytical performance of the diamond electrode for this redox species deteriorated with decreasing grain size. This shows that the properties of NCD electrodes fabricated in this manner does not support redox reaction of ferrocyanide. However, as the NCD electrode has different surface chemistry from that of MCD, it may find utility in sensing other analytes whose electrochemical reaction is usually not favored on MCD. Figure 2 (b) shows the cyclic voltammogram for 1 mM dopamine (DA) in PBS buffer, pH = 7.2 at a scan rate of 100 mV/s using an independent high-quality, hydrogen-terminated MCD electrode. As expected, its redox reaction at the MCD electrode is very sluggish with ΔE_p = 350 mV while the kinetics of Fe(CN)₆⁴⁻ at the same electrode was reversible with ΔE_p ~ 60 mV (figure 2 (a)(ii)). Detailed comparison of the electroanalytical performance of the four electrodes for sensing of DA will also be presented.

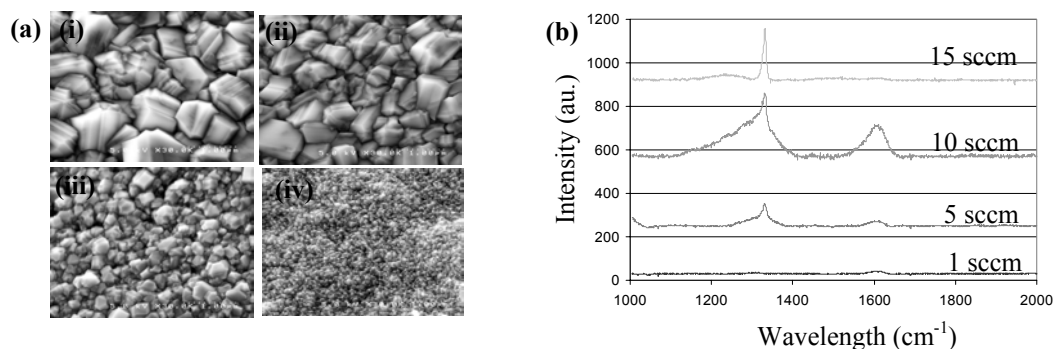


Figure 1. (a): SEM micrograph of diamond electrodes deposited at various CH₄ flow rate: (i) 15 sccm, (ii) 10 sccm, (iii) 5 sccm, and (iv) 1 sccm. TMB = 20 sccm, H₂ = 478 sccm, microwave power = 5 kW, pressure = 120 torr, temperature = 800 °C; **(b)** Raman spectra of diamond electrodes deposited with various CH₄ flow rate.

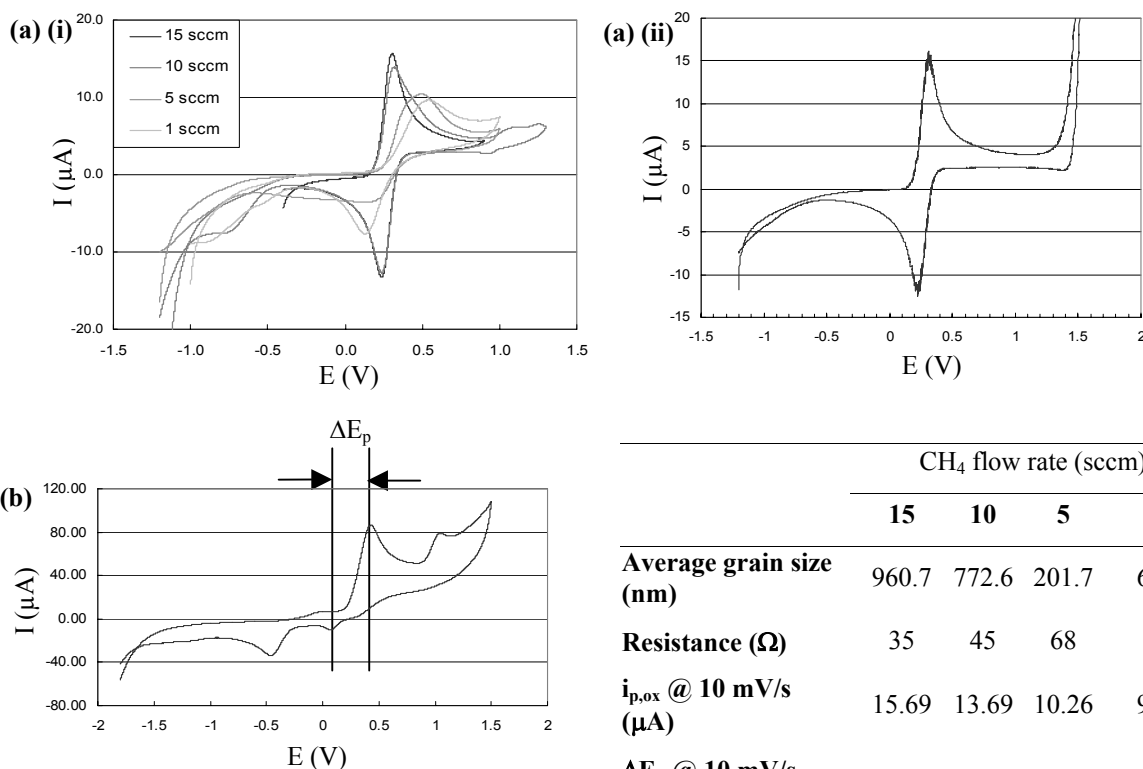


Figure 2. Cyclic voltammogram of **(a):** 1 mM Fe(CN)₆⁴⁻ in 0.1 M KNO₃ at scan rate = 10 mV/s for **(i):** diamond electrodes with various CH₄ flow rate, and **(ii):** an independent MCD electrode; **(b):** 1mM DA in PBS, pH = 7.2 at scan rate = 100 mV/s for independent MCD.

	CH ₄ flow rate (sccm)			
	15	10	5	1
Average grain size (nm)	960.7	772.6	201.7	60.5
Resistance (Ω)	35	45	68	74
i_{p,ox} @ 10 mV/s (μA)	15.69	13.69	10.26	9.34
ΔE_p @ 10 mV/s (mV)	67	77	350	406

Table 1. Effect of methane flow rate on grain size, film resistance, oxidation peak current, i_{p,ox} and peak separation, ΔE_p.

REFERENCES

1. Granger, M.C., et al., "Standard Electrochemical Behavior of High-Quality, Boron-Doped Polycrystalline Diamond Thin Film Electrode," *Anal. Chem.*, 72, 3793-3804 (2000).
2. Yarbrough, W.A.; and Messier, R., "Current Issues and Problems in the Chemical Vapor Deposition of Diamond," *Science*, Vol. 247, No. 4943, 688-696 (1990).
3. Birrell, J., et al., "Interpretation of the Raman Spectra of Ultrananocrystalline Diamond," *Diam. Relat. Mater.*, 14, 86-92 (2005).